

Mangan Oxide-assisted in Biochar Improvement and Application in Malachite Green Removal

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Abstract

The adsorption features of rice husk biochar (BC) have been improved by structure refinement due to being composited with manganese oxide (MnO). The composite material formed under low energy (temperature) was identified by X-ray Diffraction (XRD), Fourier Transform Infra-red (FTIR), and Brunauer-Emmet-Teller (BET) Surface Area instrumentation. The composite of BC/MnO analysis of XRD was specialized at 9.48° (110) and 31.42° (111). Functional group investigation of FTIR on BC/MnO composite was detected at 349 cm^{-1} and 401 cm^{-1} as manganese oxide vibration on biochar. The improvement in specific surface area is evidenced by BET surface area analysis, with the highest result at $96.047\text{ m}^2/\text{g}$. Several analyses on the adsorption work concluded that malachite green adsorption on BC/MnO composite follows the pseudo-second-order model and the Freundlich scheme under spontaneous reaction. Additionally, calculation in adsorption parameters resulted in an adsorption maximum capacity of about 79.365 mg/g with regeneration effectiveness up to 48.170% at the final of the seventh cycle.

Keywords

Biochar, Mangan Oxide, Composite, Malachite Green, Adsorption

Received: 23 April 2023, Accepted: 6 July 2023

<https://doi.org/10.26554/ijmr.2023126>

1. INTRODUCTION

In the modern era, industry activity needs huge parts in production, including dyes as an irreplaceable factor. Mass production that uses dyes in important phases disposed of unnecessary particles which might be harmful frequently. The reasons for that problem are the complex and undegradable structure of dye in the natural process, also for the reactive chemical structure that affects environmental balance. Dye wastewater pollution has become a global warning to increase eco-friendly production processes and wastewater treatment (Liu, 2020). Malachite green is commonly used in the aquaculture industry as a fungicide and parasiticide, but unfortunately, it is toxic as a contaminant (Zhou et al., 2019). Malachite green residual in water bodies has attracted food safety and environmental issue (Lin et al., 2016). Malachite green is a potential threat due to teratogenic, carcinogenic, and mutagenic for living organisms (Chang, 2017).

Wastewater treatment has attracted exciting topics to study the simplest, most effective, and cheapest (Rashid et al., 2021). Recently, adsorption has been attracted as efficient and straightforward in wastewater treatment since it has a simple way of application and varies in source adsorbent nomination. The adsorbent's controllable active site, particle size, and ion exchangeability become unique factors in adsorbent modification and

improvement (Lim et al., 2019). In a specific way, carbon-based adsorbent becomes popular due to its selectivity, excellent adsorption capacity, and thermal and chemical stability. However, it still shows drawbacks, such as high-cost production and low regeneration (Santana-Mayor et al., 2020). Popular carbon-based adsorbent includes activated carbon of charcoal, biochar, and others. Carbon-based adsorbent shows improvement challenges in high adsorption capacity and regeneration ability (Wijaya and Yuliasari, 2023).

Biochar is included as pyrogenic carbon-based material, initially generated by the pyrolysis process of biomass under an oxygen-less system. Under specific conditions of biochar production consequence of porous and rich carbon content (means full of aromatic structure). This structure has potential and utilization potential in combination with other compounds (Kumar et al., 2020). Biochar ore has limited utilization due to restricted surface charge and limited functional group (Wang et al., 2022). This limited utilization becomes a problem in biochar application as dye wastewater treatment since dyes are included as organic pollutants. Metal-based composite in biochar evidenced increasing surface characteristics and widening functional by surface properties and carbon affinity refinement in wastewater treatment (Kim and Kan, 2016; Mian and Liu, 2019). Fazal et al. (2020) successfully increased the adsorption capacity of pure biochar

up to 74.30 mg/g by compositing with TiO₂ under a calcination system at 400°C (applied to the textile wastewater). Nakarmi et al. (2020) reported on biochar optimization by compositing with ZnO and gained phosphate adsorption capacity as a pollutant up to 265.5 mg/g. Jiang et al. (2018) reported on biochar/Al₂O₃ composite formation and reached an adsorption capacity of up to 196.1 mg/g toward fluoride as a pollutant.

Current work reported improving rice husk-based biochar by compositing with manganese oxide under a low energy (temperature) scheme. Removal dye wastewater ability was examined in malachite green (MG) contamination. XRD, FTIR, and BET instrumentation analyzed material characteristics. The regeneration ability was studied in seven cycles of MG adsorption-desorption.

2. EXPERIMENTAL SECTION

2.1 Chemicals and Instrumentation

This work used biochar (BC) produced by pyrolysis of rice husk biomass at 500°C. The pro-analysis chemicals as a precursor in this work were potassium permanganate (KMnO₄; purchased from Merck), manganese (II) acetate tetrahydrate ((CH₃COO)₂Mn. 4H₂O; purchased from Sanche), sodium chloride (NaCl; purchased from Sigma Aldrich), hydrochloride acid (HCl 37%; purchased from Mallinckrodt AR), sodium hydroxide (NaOH; purchased from Merck), powder dye of malachite green/MG (C₂₃N₂H₂₅Cl; purchased from CV. Agung Menara Abadi), and aquadest (purchased from PT. Brataco). Biochar-modified materials were characterized using several instruments such as X-Ray Diffraction (XRD) Rigaku Miniflex-6000 with a scan range of 2θ 5-80°, Fourier Transform Infra-red (FT-IR) spectroscopy Prestige-21 with a scan range of wavenumber 450-3800 cm⁻¹, surface area analyzer based on Brunauer-Emmett-Teller (BET) method Quantachrome NOVA-4200, and Ultra Violet-Visible spectroscopy of Biobase BK-UV 1800 PC by wavelength measurement at 617 nm.

2.2 Composite BC/MnO Preparation

BC powder (15 g) and KMnO₄ (3.16 g) were dissolved to aquadest (150 mL) under room temperature, and that suspension was sonicated for 30 minutes. The suspension was added stepwise by 0.3 M of (CH₃COO)₂Mn.4H₂O solution (100 mL) under heating conditions of 80°C. The final suspension was aged 30 minutes and washed thrice with aquadest. The biochar-modified precipitate was oven dried at 80°C.

2.3 Adsorption Works

The adsorption works were carried out by observing the optimum pH pzc (point of zero charge), pH adsorption, adsorption time, starting concentration, and temperature variation parameters using 0.02 g adsorbent. The pH pzc parameter measured the adsorption ability of materials in varying pH values (in the range of 2-11) of 20 mL sodium chloride solution (0.1 M) for 120 minutes of adsorption time. The optimal pH on dye adsorption was observed by varying the pH value (in the range of 2-11) of 20 mL MG solution (30 mg/L) for 120 minutes adsorption process. pH variation was controlled using HCl and NaOH solution (0.1 M). The effect of adsorption time was examined by preparing

0.02 g adsorbent in 20 mL MG solution (50 mg/L) for varying time (0-240 minutes). The effect of starting concentration and temperature variation was carried out using 20 mL MG solution, varying the dye concentration of 30-80 mg/L, and varying the temperatures of 30-70°C for 60 minutes adsorption process.

2.4 Regeneration Works

The regeneration work was done by an adsorption-desorption scheme using 20 mL MG dye solution (60 mg/L) for seven cycles, repeatedly. Every cycle of adsorption was done under 120 minutes adsorption process; then desorption was done using the aquadest solvent in the sonication bath. The remaining concentration of every cycle adsorption was measured using a UV-Vis spectrophotometer.

2.5 Analysis and Calculation

Several formula analyses were used to approve the conclusion of the adsorption analysis. The amount of MG particulate adsorbed was calculated by the formula (1):

$$q_t = \frac{C_0 - C_t}{W} V \quad (1)$$

C₀ and C_t are noticed as the amount of particulate that is adsorbed at an initial and specific time (mg/L). V and W are noticed as volume (L) of wastewater used and adsorbent dose (g), respectively.

Parameters of kinetic were measured according to pseudo-first-order (PFO) and pseudo-second-order (PSO) models in Equations (2) and (3):

$$\log(q_t - q_e) = \log q_t - \frac{K_1 - t}{2.303} t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_t^2} + \frac{1}{q_t} \quad (3)$$

q_t and q_e represent the amount of dye particulate adsorbed at a specific time and equilibrium condition (mg/g). K₁ and K₂ are represented as constants of the PFO and PSO models.

Isotherm parameters were calculated according to Langmuir and Freundlich's models. Equations (4) and (5) were represented for Langmuir and Freundlich, respectively, as below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where q_{max} and q_e are the amount of dye particulate adsorbed at maximum and equilibrium conditions (mg/g), respectively. C_e has represented the dye wastewater concentration at equilibrium

adsorption (mg/L). K_L and K_F are represented as the Langmuir constant (mg/L) and Freundlich constant (L/g).

Thermodynamic parameters are calculated according to Equations (6), (7), and (8) as below:

$$\Delta G^\circ = -RT \cdot \ln K_d \quad (6)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

$$K_d = \frac{q_e}{R} - \frac{q_e}{C_t} \quad (8)$$

Where K_d is represented as the coefficient of adsorption distribution, C_t is represented as dye concentration at equilibrium condition (mg/L). R and T are gas constant and absolute temperature (K).

3. RESULTS AND DISCUSSION

BC base and BC/MnO materials were initially characterized using XRD, FTIR, and BET to confirm the formed result, especially in crystallinity, functional group composition, and surface area changes aspects (Siregar et al., 2021; Wijaya and Yuliasari, 2023). XRD analysis is plotted in Figure 1, which is figured the specific peak of MnO structure at 9.48° (110) and 31.42° (111) of 2θ (according to JCPDS number 44.0141) in BC structure ((002), identified by peak at 24.12° of 2θ as high organic content material) (Gangwar and Rath, 2021; Juleanti et al., 2021). Increasing peak intensity at 31.42° (111) is identified as the monoclinic shape of the MnO structure, which is composited with the -OH part of the carbon structure (MnOOH) of biochar-based material (Wei et al., 2012).

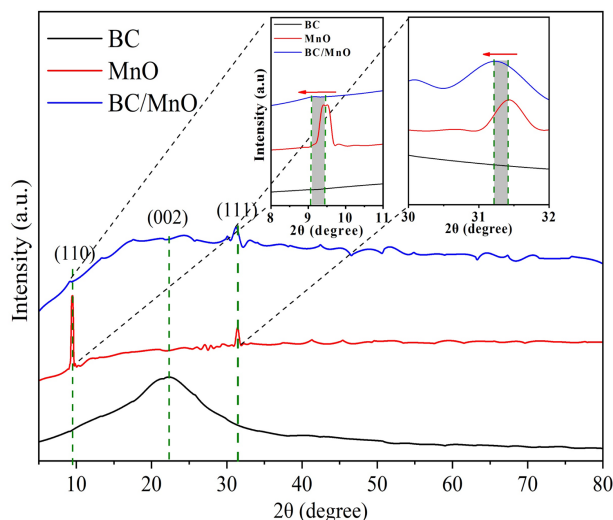


Figure 1. XRD Plots of Biochar-based Material

FTIR analysis identified the functional group formation for biochar-based composite with MnO (see Figure 2). The FTIR spectrum in Figure 2 shows biochar's unique functional group in composite BC/MnO, such as wide-band peak at 3448.72 cm^{-1} as -OH stretching, 1620.21 cm^{-1} as C=C bending, and 1103.28 cm^{-1} as hydroxyl bending to C-O functional group (Hamid et al., 2022). According to Gangwar and Rath (2021), the carbonyl functional group at 3448.72 cm^{-1} , 11620.21 cm^{-1} , and 1103.28 cm^{-1} in biochar was detected as MnO's stretching and bending vibration. Furthermore, a specific spectrum at low wavenumber as metal-based vibration bending was noticed at 349 cm^{-1} and 401 cm^{-1} as MnO vibration with the carbon structure of rice husk biochar (Rani et al., 2023).

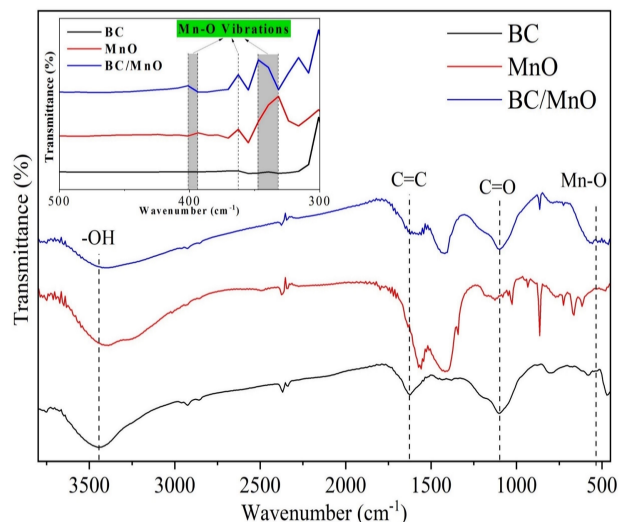


Figure 2. FTIR Spectrums of Composited Biochar Adsorbent

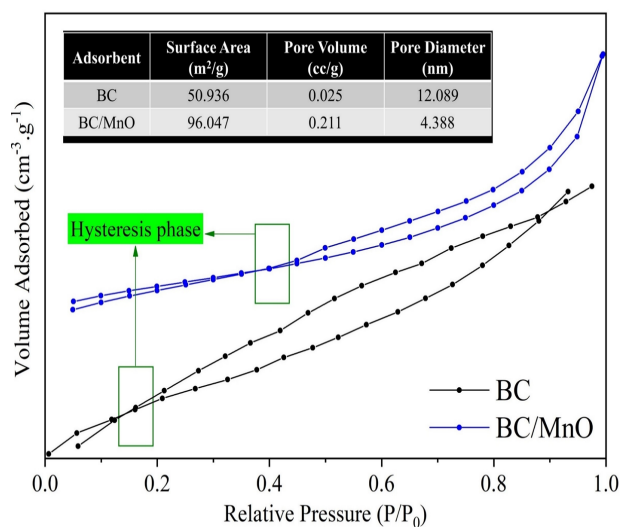


Figure 3. BET Analysis Profile of Unmodified Biochar and Composited Biochar

Table 1. Data of Kinetic Parameter for MG Adsorption

Adsorbent	Initial Concentration (mg/L)	$Q_{experiment}$ (mg/g)	PFO			PSO		
			Q_{e-calc} (mg/g)	R^2	K_1	Q_{e-calc} (mg/g)	R^2	K_2
BC	50	25.836	15.678	0.927	0.015	27.173	0.9969	0.00205
BC/MnO		41.634	32.277	0.977	0.021	45.454	0.9983	0.00102

Table 2. Data of Isotherm Parameters for MG Adsorption

Adsorbent	Temperature (°C)	Model of Isotherm Adsorption					
		Langmuir			Freundlich		
		Q_{max}	K_L	R^2	n	K_F	R^2
BC	30	61.728	0.074	0.9409	0.051	2.023	0.9749
	40	24.450	0.137	0.9469	0.718	3.433	0.9665
	50	25.253	0.147	0.9111	0.768	2.252	0.970
	60	26.738	0.174	0.836	0.093	8.892	0.944
	70	28.090	0.195	0.7312	4.688	2.551	0.864
BC/MnO	30	77.519	0.204	0.862	0.407	6.483	0.990
	40	79.365	0.224	0.859	0.052	2.168	0.967
	50	76.336	0.327	0.912	0.116	9.093	0.946
	60	75.188	0.484	0.955	0.116	2.336	0.943
	70	74.627	0.912	0.980	0.410	3.442	0.921

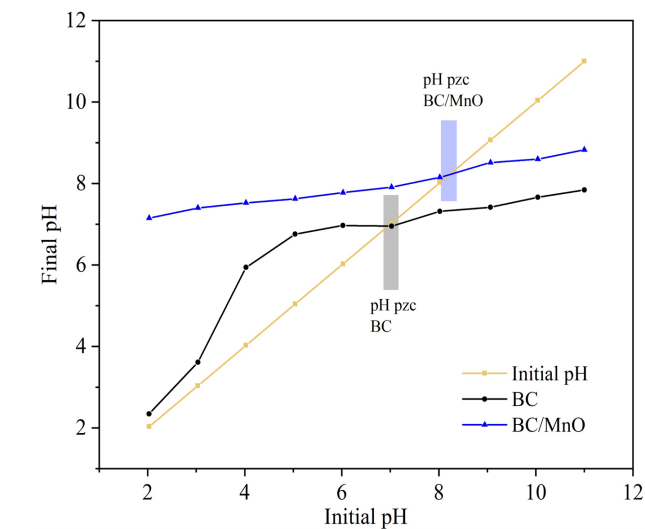


Figure 4. pH PZC Dependent of Composited Biochar

Surface area analysis of BC/MnO composite using BET model isotherm calculation with plot N₂ isotherm adsorption is shown in Figure 3. According to the plot result in Figure 3, the adsorption-desorption graphs generate a hysteresis loop that fits type IV hysteresis type (Hakim et al., 2023b). Graph of adsorption-desorption process figuring broad body-narrow edge form (H₂-type) that explains the gas capillary condensation in the mesopore

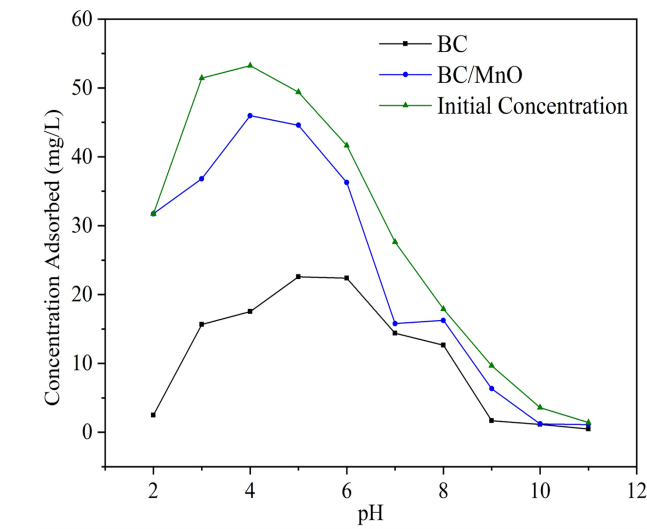


Figure 5. pH-Dependent in MG Adsorption Using Composited Biochar

re at relatively high-pressure conditions (Cychosz and Thommes, 2018). Composite formation on rice husk biochar with MnO enhanced surface area structure from 50.936 m²/g to 96.047 m²/g. This mean particle structure re-composition was reached for a miniature size version, and a pore structure refinement occurred (Monakhova et al., 2021).

Table 3. Analysis Results of Thermodynamic Parameters for MG Adsorption

Adsorbent	Concentration (mg/L)	T (°C)	Q _e (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol)
BC	30	30	8.031	15.584	0.043	2.504
		40	9.627			2.072
		50	10.599			1.641
		60	11.781			1.209
		70	13.065			0.777
	40	30	17.553	12.434	0.039	0.654
		40	19.078			0.265
		50	20.106			-0.124
		60	21.781			-0.512
		70	23.370			-0.901
	50	30	27.391	11.209	0.039	-0.464
		40	29.127			-0.849
		50	30.373			-1.235
		60	32.199			-1.620
		70	33.543			-2.005
	60	30	38.927	12.368	0.045	-1.214
		40	39.537			-1.662
		50	48.304			-2.111
		60	48.356			-2.559
		70	49.133			-3.007
	70	30	43.148	9.098	0.034	-1.117
		40	45.746			-1.454
		50	52.225			-1.791
		60	58.848			-2.129
		70	59.172			-2.466
	80	30	42.071	7.843	0.027	-0.475
		40	62.146			-0.749
		50	59.089			-1.024
		60	53.155			-1.298
		70	76.945			-1.573
BC/MnO	30	30	19.831	9.743	0.037	-1.516
		40	20.094			-1.888
		50	20.901			-2.260
		60	21.755			-2.631
		70	22.584			-3.003
	40	30	28.683	13.439	0.052	-2.226
		40	29.439			-2.743
		50	30.554			-3.260
		60	31.787			-3.777
		70	32.991			-4.294
	50	30	38.727	17.738	0.068	-2.892
		40	39.539			-3.573
		50	40.761			-4.254
		60	43.006			-4.935
		70	44.146			-5.616
	60	30	48.727	20.241	0.078	-3.416
		40	49.701			-4.197
		50	51.117			-4.978
		60	52.858			-5.758
		70	55.193			-6.539
	70	30	59.704	21.431	0.084	-4.060
		40	60.870			-4.901
		50	62.346			-5.743
		60	63.862			-6.584
		70	66.263			-7.425
	80	30	61.702	11.468	0.048	-2.948
		40	63.339			-3.423
		50	64.522			-3.899
		60	65.971			-4.375
		70	68.534			-4.851

Table 4. Current Status of Biochar-based Adsorbent Improvement with Manganese Compound

Biochar Type	Treatment/modification	Pollutant Type	Adsorption Capacity (mg/g)	References
Rice husk/MnO _x	Vacuum dried @90°C; furnace @600°C with N ₂	Cr(VI)	28.58	(Fan et al., 2022)
Potato steam & leaves/Fe/MnO _x	Composited with Fe; oven-dried @500°C less O ₂	Ciprofloxacin	8.37	(Li et al., 2018)
		Enrofloxacin	7.19	
		Norfloxacin	6.94	
Rice husk/nano MnO ₂	Oven-dried @80°C under N ₂ atmosfer	Tetracycline	25.50	(Li et al., 2020)
		Doxycycline	31.34	
Corn straw/MnO	Pyrolysis @600°C with N ₂ ; oven-dried 4 hours	Arsenic	14.3618	(Yu et al., 2015)
Rice husk/MnO	Oven-dried @80°C	MG dye	68.534	This work

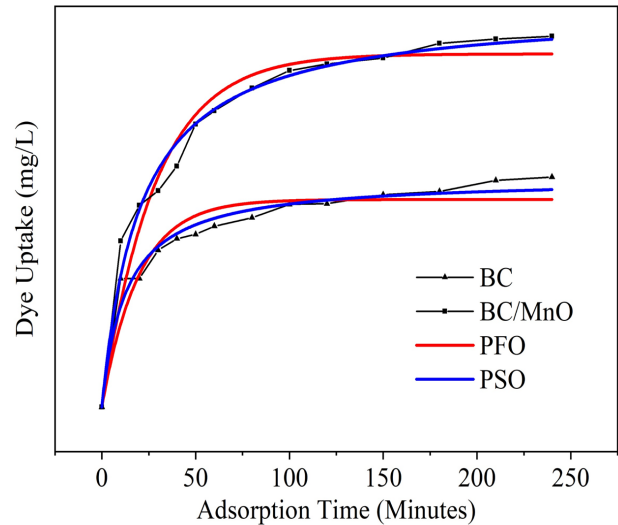


Figure 6. Kinetic Adsorption Analysis on Composited Biochar

The pH pzc material is preliminary examined to find out about the surface neutral charge in composite material. According to Figure 4, the pH pzc of BC/MnO composite is located at pH 8, meaning composite material has no charge in alkaline conditions (Fan et al., 2022). According to Priatna et al. (2023), a condition under pH pzc will generate a positive charge on material surfaces and vice versa. Next, pH optimum adsorption analysis showed MG adsorption on BC/MnO composite occurred at a pH of 4 (see Figure 5). The pH optimum adsorption is verified by the correlation surface charge of BC/MnO composite to MG adsorption, and it was expected that adsorption of MG with BC/MnO composite dominated by hydrogen bonding formation. Hydrogen bonding is expected between the MG dye’s charge and the biochar’s carbon structure (Abubakar and Batagarawa, 2017). On the other hand, the high adsorption ability of BC/MnO to MG

dye is also affected by the π - π interactions from the aromatic structure of MG and biochar-based material (Tsai et al., 2022).

The kinetic parameter of MG adsorption using BC/MnO composite was analyzed by pseudo-first-order (PFO) and pseudo-second-order (PSO) model equations. Figure 6 shows the comparison of MG adsorption to unmodified biochar and composited biochar. Both adsorbents follow the PSO kinetic adsorption model, meaning the adsorbate interaction with the adsorbent is dominated by the chemisorption scheme (Hakim et al., 2023a). Table 1 shows the calculation result of the PFO-PSO model. Data in Table 1 confirmed the MG adsorption fitted with the PSO model according to the R^2 value closest to 1.

Isotherm and thermodynamic parameters were calculated by temperature variation and starting concentration data. Figure 7 shows the trend correlation between increasing in concentration and temperature to the adsorption capacity of the adsorbent. The isotherm adsorption parameter was analyzed using Langmuir and Freundlich’s model based on starting concentration adsorption (Freundlich, 1907; Langmuir, 1916). Table 2 shows calculated data by Langmuir and Freundlich’s model equation. According to the R^2 value closest to 1, MG adsorption using both biochar-based adsorbents under different temperatures follows the Freundlich model, which is expected to be dominated by a multilayer adsorption scheme (physisorption). The Langmuir is distinguished from Freundlich models according to the adsorption scheme that occurs by monolayer in Langmuir (directly adsorbate to adsorbent) and multilayer in Freundlich (growth in heterogeneous places) (Hakim et al., 2023b). The current status of several biochar-based adsorbents (this work compared to others) improved by composite formation using manganese precursor, according to Table 4.

Thermodynamic adsorption parameter was analyzed by the temperature variation to provide enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) data (Motomura, 1978). All of those data were calculated according to Equations (6)-(8), and the

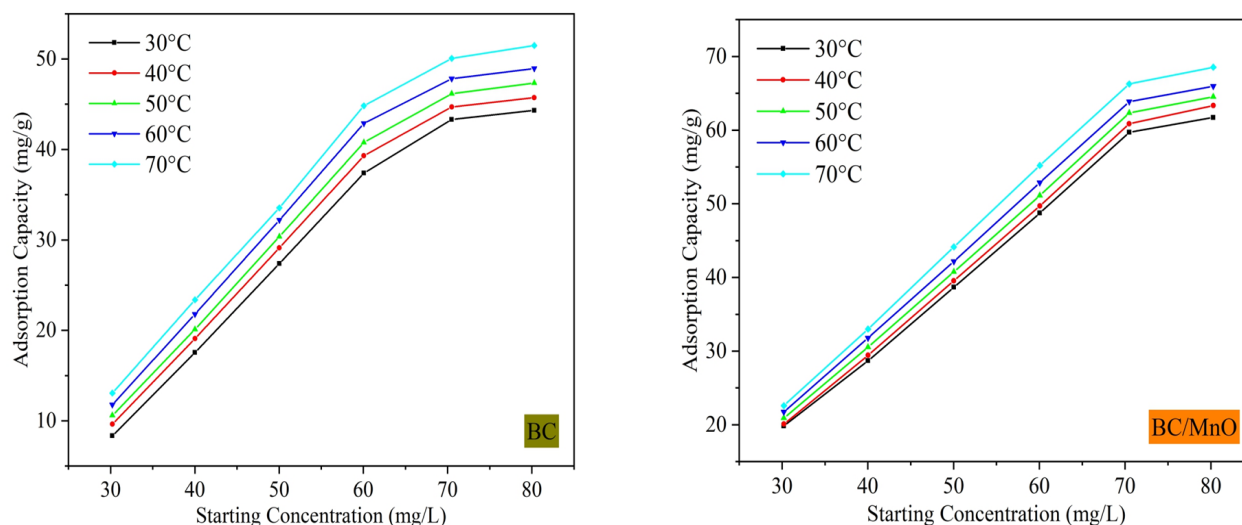


Figure 7. Plot Analysis of Temperature and Concentration Parameters on MG Adsorption Using Composited Biochar

calculated results were plotted in Table 3. The positive value of ΔH and ΔS indicate that the adsorption feasible occurred endothermically under high temperatures. The spontaneous adsorption scheme also provides a negative value of ΔG (Hakim et al., 2023a; Siregar et al., 2022; Sahmoune, 2019). The effect of thermodynamic parameters on material features was controlling the adsorption capacities. It will increase aligned with temperature improvement due to controllable repulsive forces under high-temperature conditions. This description was supported by decreasing pattern of ΔG value (Malima et al., 2021).

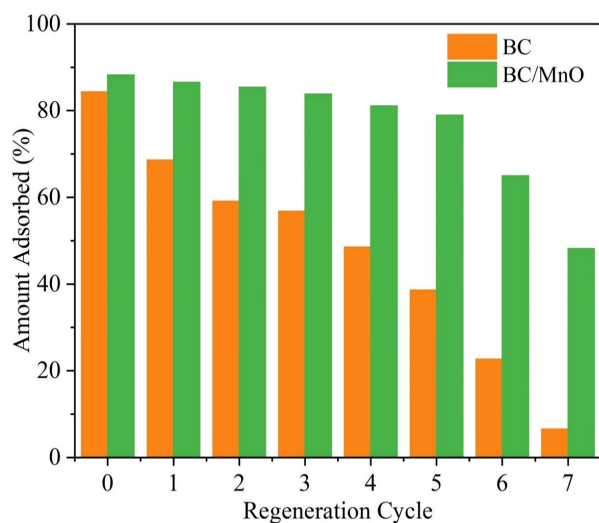


Figure 8. Regeneration Ability of Composited Biochar

Regeneration works evidenced the effectiveness of MG adsorption on the composited biochar for seven cycles. The final cycle experiment (7th cycle) still effectively decreases MG dye concentration to 48.17% (see Figure 8). The regeneration works reached by adsorption-desorption mechanism using aquadest as

a solvent and ultrasonic instrument to ensure the disintegration of dye absorbed from adsorbent by physical bonding termination (Daghooghi-Mobarakeh et al., 2022). This condition expected a sufficient simple way to regenerate biochar-based adsorbent using a water-based solvent. Then this shows a better prospect for utilizing carbon-based biomass as an adsorbent agent in water remediation.

4. CONCLUSIONS

The biochar produced from rice husk biomass has improved the adsorption ability by combination with MnO under a low-temperature preparation scheme. The physicochemical characterization using XRD showed the combination of peak biochar to MnO as the composite mark. FTIR analysis confirmed the Mn-bonding to carbon structure of biochar (see the spectrum at 300-400 cm^{-1}). The specific surface area of composited biochar was improved to 96.047 m^2/g . The adsorption work using composited biochar was optimal for 180 minutes, and the capacity adsorption reached 68.534 mg/g under a pH value of 4. The regeneration work of the pristine biochar and the composited one evidenced the effectiveness of seventh cycles adsorption toward MG dye wastewater.

5. ACKNOWLEDGEMENT

The authors acknowledge the instrumentation support from the Research Center of Inorganic Materials and Coordination Complexes, Sriwijaya University.

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